Bridgman's phase diagram<sup>3</sup> shows that only  $\alpha$  thallium (h.c.p.) should be expected in these experiments. However, quenched  $\beta$ thallium (f.c.c.) is stable at room temperature.<sup>4</sup> An elongated

TABLE I. Summary of data on the effect of hydrostatic pressure on the superconducting transition of tin and thallium.<sup>a</sup>

| Pressure<br>(atmos) | $\Delta T_c$ (°K)   | $(\Delta T_c/\Delta P) \times 10^{5}$<br>deg atmos <sup>-1</sup>   |
|---------------------|---|--|
| For tin             |   |  |
| 95<br>82°           | -0.0027<br>-0.007   | $-3 -8.6^{\circ}$  |
| 210                 | -0.001  | -5   |
| 1730                | -0.10   | -5.8   |
| 11 500              | -0.52   | -4.3   |
| 17 500              | -0.8  | 4.5  |
| 60°                 | -0.0034   | -5.5°  |
| <115                |   | $-4.9 \pm 0.5$   |
| for thallium        |   |  |
| 1370                | 0.008   | 0.6  |
| 1730                | 0.025   | 1.4  |
| 13 400              | -0.06   | -0.4   |
| <48                 |   | $1.3 \pm 0.2$  |
|                     | $\begin{array}{c} \mbox{Pressure} \\ (atmos) \\ \mbox{For tin} \\ \mbox{95} \\ \mbox{826} \\ \mbox{827} \\ \mbox{11} \\ \mbox{100} \\ \mbox{11500} \\ \mbox{11500} \\ \mbox{11500} \\ \mbox{11500} \\ \mbox{100} \\ \mbox{11500} \\ \mbox{100} \\ \mbox{11700} \\ \mbox{117300} \\ \mbox{117300} \\ \mbox{117300} \\ \mbox{113400} \\ \mbox{<48} \end{array}$ | $\begin{array}{c c} \mbox{Pressure} & \Delta T_{\rm e} \\ (atmos) & \Delta T_{\rm e} \\ \mbox{(°K)} \\ \hline \mbox{For tin} & & & \\ \mbox{95} & -0.0027 \\ \mbox{82°} & -0.007 \\ \mbox{21°} & -0.001 \\ \mbox{1730} & -0.10 \\ \mbox{11} & 500 & -0.52 \\ \mbox{17} & 500 & -0.8 \\ \mbox{60°} & -0.0034 \\ \mbox{<115} \\ \hline \mbox{for thallium} \\ \mbox{1370} & 0.008 \\ \mbox{1730} & 0.025 \\ \mbox{13400} & -0.06 \\ \mbox{<48} \\ \end{array}$ |

<sup>a</sup> Presented at the Third International Conference on Low Temperature Physics and Chemistry, Houston, Texas, December 17, 1953.
<sup>b</sup> G. J. Sizoo and K. Onnes, Leiden Comm. No. 180b (1925).
<sup>c</sup> Hydrostatic value deduced from tensile stress.
<sup>d</sup> N. E. Alekseyevsky, J. Exptl. Theoret. Phys. (U.S.S.R.) 10, 746 (1940).
<sup>e</sup> Kan, Lazarev, and Sudovstov, Doklady Akad. Nauk. 69, 173 (1949).

<sup>4</sup> See reference 2.
 <sup>5</sup> Grenier, Spöndlin, and Squire, Physica 19, 833 (1953).
 <sup>b</sup> See reference 1.

specimen selected from particles produced by pouring molten thallium into liquid nitrogen had the same characteristics as previous samples.

These measurements, which will be reported in detail later, are being continued on specimens for which the crystal structure is known, using apparatus permitting appreciable increased accuracy of determination of the pressure coefficients at zero pressure.

<sup>1</sup> Kan, Lazarev, and Sudovstov, J. Exptl. 1 heoret. Flys. ( 825 (1948). <sup>2</sup> P. F. Chester and G. O. Jones, Phil. Mag. 44, 1281 (1953). <sup>3</sup> P. W. Bridgman, Phys. Rev. 48, 893 (1935). <sup>4</sup> S. Sekito, Z. Krist. 74, 189 (1930). Lazarev, and Sudovstov, J. Exptl. Theoret. Phys. (U.S.S.R.) 18,

## Resistivity Changes in Copper, Silver, and Gold Produced by Deuteron Irradiation Near 10°K\*

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PREVIOUS research<sup>1,2</sup> on various metals indicates that radiation damage introduced near liquid nitrogen temperature will anneal when held at the irradiation temperature. The present experiment was designed to obtain damaged specimens in which no thermally activated motion of the lattice defects occurs during irradiation.

 $99.97 \pm 0.02$  percent pure wires of copper, silver, and gold were irradiated with 12-Mev deuterons. The wire diameters were 5 mils for the copper and silver and 4 mils for the gold. The maximum temperature during bombardment was 12°K for the first run and

TABLE I. Radiation-induced resistivity increases, in units of  $10^{-7}$  ohm cm, after a flux of  $10^{17}$  deuterons/cm<sup>2</sup>.

|   | Point                                | Copper | Silver | Gold |
|---|--------------------------------------|--------|--------|------|
| A | extrapolating<br>initial 12°K slope  | 2.3    | 2.6    | 3.8  |
| B | (observed 12°K value)                | 1.9    | 2.0    | 3.1  |
| С | extrapolating<br>initial 135°K slope | 0.9    | 1.4    | 2.6  |
| D | (observed 135°K value)               | 0.6    | 1.0    | 1.9  |

16°K for the second. Even though the temperature difference was small, the resistivity versus deuteron flux curves for the second run all lie slightly below those of the first.

If the initial slope of the resistivity versus flux curves was valid up to large flux, the resistivity increases produced in copper, silver, and gold after 1017 deuterons per cm<sup>2</sup> would be those given as point A in Table I. However a slight decrease in slope does occur and the observed increases are those denoted as point B. These changes are to be compared with the point C and D values obtained<sup>1</sup> with 12-Mev deuteron irradiation at  $135^{\circ}$ K, where point C represents the values obtained by extrapolating the initial slope to a flux of  $10^{17}$  deuterons/cm<sup>2</sup> and point D the observed values for this flux.

After bombardment the specimens were allowed to warm, first to liquid nitrogen temperature and then to room temperature. The warmup rate was between 15 and 30°C per hour. The annealing out of damage during warmup was obtained by using a similar unbombarded specimen in a Wheatstone bridge circuit<sup>2</sup> so that the resistivity introduced by thermal oscillations can be eliminated if the two specimens are at the same temperature. Corrections for temperature differences of specimen and dummy were obtained by comparison with warmups made before irradiation and after annealing to room temperature.

On holding for 48 hours at or slightly below the bombardment temperature, no change in resistivity (i.e., to  $\pm 0.1$  percent) was observed. In copper and silver, abrupt drops in resistivity indicated that some rather unique annealing process occurred at about 40°K and 30°K, respectively. In gold no large low-temperature drops were found. The first two rows in Table II indicate the

 TABLE II. Percentage of initial resistivity increase remaining after annealing to various temperatures.

| Annealing<br>temperature | Copper | Silver | Gold |
|--------------------------|--------|--------|------|
| 35°K                     | 90     | 78     | 97   |
| 45°K                     | 50     | 77     | 93   |
| 77°K                     | 41     | 69     | 86   |
| 220°K                    | 25     | 32     | 55   |
| 300°K                    | 7      | 10     | 10   |
| 300°K                    |        | 10     |      |

magnitude of these processes and the third gives the percentage left after annealing to liquid nitrogen. Two possible processes that may explain these abrupt recoveries are the motion of interstitial atoms, which Huntington<sup>3</sup> calculated would have an activation energy in the range 0.07 to 0.24 ev, or the recombination of very close interstitial-vacancy pairs as suggested previously.<sup>1,2</sup>

A gradual decrease occurs in all three materials during the warmup to 220°K and then a more rapid process becomes important.<sup>1,2</sup> The latter process is complete at about 255°K in copper, at approximately 240°K in silver, and at roughly 285°K in gold. The percentage remaining at both 220°K and 300°K is given in Table II.

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<sup>1</sup> Marx, Cooper, and Henderson, Phys. Rev. 88, 106 (1952).
<sup>2</sup> A. W. Overhauser, Phys. Rev. 90, 393 (1953).
<sup>3</sup> H. B. Huntington, Phys. Rev. 91, 1092 (1953).

## Line-Narrowing by Macroscopic Motion

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THE investigation of nuclear magnetism often demands extremely high resolution. A notable example is furnished by the structure in the groups of proton resonance lines discovered by Arnold and Packard.<sup>1</sup> The separation of the three components of

the CH<sub>3</sub> group in ethyl alcohol amounts to only about 6 cycles per second and requires for its resolution a homogeneity of the external field over the sample region to within about one milligauss. In a typical field of 7000 gauss this represents a resolution of one part in 7 millions which can be achieved with considerable care.

It is tempting, however, still to increase the resolution at least tenfold in order to observe further interesting details. While it would seem very difficult to obtain a field of sufficient homogeneity, it is possible to reach this goal in a rather simple way, i.e., by providing a motion of the substance within the sample under investigation.

The mechanism can be qualitatively understood by assuming that the external field varies over the sample by an amount of the order  $\Delta H$  and that a given molecule participates in the macroscopic motion of the substance in a manner such that, during each time interval of the order t, it is once exposed to the range of variation  $\Delta H$  of the magnetic field. The more rapid the motion, i.e., the shorter the interval t, the more a nucleus in the molecule reacts as if it were exposed all the time to the average value of the field. It can be shown that the effect will start to become appreciable if

$$t \cong 2\pi/(\gamma \Delta H), \tag{1}$$

where  $\gamma$  is the gyromagnetic ratio of the nucleus under consideration. As an example we consider protons in an external field which varies over the sample by the amount  $\Delta H \cong 2 \times 10^{-3}$  gauss. To obtain an effective averaging of this field, one has to demand, according to Eq. (1), that the time t be less than about  $\frac{1}{10}$  sec. In a sample with linear dimensions of  $\frac{1}{2}$  cm this requires a speed somewhat higher than 10 cm/sec, which is certainly well within the realm of mechanical possibilities.

It must be noted that formula (1) implies that every molecule in the substance experiences the full range of variation  $\Delta H$  during the time interval t. Generally, however, the averaging process will take place for each molecule only over those regions of the sample through which it is carried in the course of its motion. As a result one will observe a partial narrowing of the line which, however, can be very appreciable under suitable circumstances.

A more quantitative treatment of the effect is obtained from the phenomenological equations of nuclear induction.<sup>2</sup> Assuming, for example, that the motion within the substance has the effect of exposing a given molecule, after a mean time  $\theta$ , to a randomly different field within the sample, one obtains for short  $\theta$  a reduction of the field inhomogeneity to an "effective value"

$$(\Delta H)_{\rm eff} = \gamma \langle (\Delta H)^2 \rangle_{\rm AV} \theta, \qquad (2)$$

where  $\langle (\Delta H)^2 \rangle_{AV}$  is the mean square deviation of the field in the sample from its average value. Irrespective of the manner in which the external field varies over the sample, one obtains in this case a "Lorentzian" line with an "effective" transverse relaxation time

$$(T_2)_{\text{eff}} = 1/[1/T_2 + \gamma(\Delta H)_{\text{eff}}], \qquad (3)$$

where  $T_2$  is the transverse relaxation time due to natural broadening.

<sup>1</sup> This structure is distinguished from the one reported earlier by Arnold, Dharmatti, and Packard [J. Chem. Phys. **19**, 507 (1951)] where the OH, CH<sub>2</sub>, and CH<sub>3</sub> groups in ethyl alcohol were shown to lead to separate resonances. Higher resolution reveals that each of these resonances consists of a number of closely spaced lines. These more recent findings will soon be published. of a number of care published. <sup>2</sup> F. Bloch, Phys. Rev. 70, 460 (1946).

## A Line-Narrowing Experiment

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HE possibility of line narrowing by macroscopic motion of the material within a sample, described in the foregoing letter, has been experimentally established. A nuclear induction apparatus consisting of a 7000-gauss permanent magnet and the



FIG. 1. Line narrowing by rotation. The top figure is a photograph of a proton resonance from distilled water displayed on the cathode-ray screen. The beam was swept from right to left in about 30 seconds. A measure of the external field inhomogeneity is given by the width at half-maximum and was found to be  $1.7 \times 10^{-3}$  gauss. The bottom figure was obtained by rotating the spherical sample at a rate of about 25 times per second, but under otherwise identical conditions. The variation of the field between the two ends of this trace was determined by calibration to be  $3.5 \times 10^{-3}$  gauss, yielding for the width at half-maximum and bout  $10^{-4}$  gauss. This reduction in half-width is accompanied by an increase of the height by a factor of about 7. about 7.

associated radio-frequency components was used. The magnet was shimmed to give a homogeneity within about 10<sup>-3</sup> gauss over a spherical sample of  $\frac{3}{16}$ -inch diameter.

A simple and effective way to induce a macroscopic motion was found to be a rotation of the entire sample about an axis (y), coincident with the axis of the receiver coil. This method achieves a partial narrowing in the sense that it effects an averaging over the field around coaxial circles in the plane normal to this axis. It has been possible in this manner to narrow the line appreciably and thereby increase its height with rotational speeds in excess of about 10 cycles per second. This is in agreement with the order of magnitude of the time t, referred to in the previous letter. The samples were enclosed in a shaft extending into the receiver coil. This shaft was driven by a small air turbine located above the head.

The figure shows oscilloscope traces of proton resonance lines in distilled water with and without rotation of the sample. It is seen that the rotation of the sample results in a reduction of the halfwidth by a factor of about 17 and an increase of the maximum by a factor of 7. The fact that the areas under the two curves do not seem to agree is possibly due to partial saturation in the case of the narrower line.

Since simple rotation averages only along coaxial circles, the best over-all homogeneity for the stationary samples will not necessarily represent the optimum field configuration under rotation. For example, in the best over-all field there may be a comparatively strong variation in the y direction over which no averaging takes place in the present arrangement. Thus the